PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SEIDOU KAGAKU KOGYO KK
(72)Inventor : YOSHIKAWA CHIKAHITO
WAKE YUMIKO
MAHANA AIKO

(54) POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a positive electrode active material with a cycle life characteristic superior in charging/discharging and a nonaqueous electrolyte secondary battery using it.
SOLUTION: This positive electrode active material is represented by the expression Li1+xMn2-x-y-zAyBzO4, and this nonaqueous electrolyte secondary battery uses it. In the expression A is at least one element selected from Co, Ni, Fe and Cr, B is at least one element selected from Mg and Ca and x, y and z are set in the respective ranges of $0 \leq X \leq 0.09$, $0.01 \leq y \leq 0.3$, $0.01 \leq z \leq 0.3$.

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4/02		4/02	Ｃ	５Ｈ０１４
10/40		10/40	Ｚ	５Ｈ０２９

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(21)出願番号　特願平10－225439

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(71)出願人　593078615
正同化学工業株式会社
大阪府大阪市中央区北浜二丁目１番26号
(72)発明者　吉川　周仁
兵庫県赤穂市中広1576　正同化学工業株式会社内
(72)発明者　和氣　由美子
兵庫県赤穂市中広1576　正同化学工業株式会社内
(74)代理人　100081536
弁理士　田村　巌

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(54)【発明の名称】　正極活物質及びこれを用いた非水電解液二次電池

(57)【要約】
【課題】　充放電でのサイクル寿命特性の優れた正極活物質及びこれを用いた非水電解液二次電池を提供する
【解決手段】　下記式で表される正極活物質及びこれを用いた非水電解液二次電池。
$Li_{1+x}Mn_{2-x-y-z}A_yB_zO_4$
A＝Co，Ni，Fe，Crから選ばれる少なくとも１つの元素
B＝Mg，Zn，Caから選ばれる少なくとも１つの元素
$0 \leq x \leq 0.09$、$0.01 \leq y \leq 0.3$、$0.01 \leq z \leq 0.3$

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【特許請求の範囲】
【請求項１】　下記式で表される正極活物質。
$Li_{1+x}Mn_{2-x-y-z}A_yB_zO_4$
A＝Co，Ni，Fe，Crから選ばれる少なくとも１つの元素
B＝Mg，Zn，Caから選ばれる少なくとも１つの元素
$0 \leqq x \leqq 0.09$、$0.01 \leqq y \leqq 0.3$、$0.01 \leqq z \leqq 0.3$
【請求項２】　請求項１の正極活物質を用いる非水電解液二次電池。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は改良された正極活物質、これを用いた非水電解液二次電池に関する。
【０００２】
【従来の技術】非水電解液二次電池は、例えば負極にリチウム、リチウム化合物、リチウム合金等を用い、電解液として炭酸プロピレン（ＰＣ）、１，２－ジメトキシエタン（ＤＭＥ）、γ－ブチロラクトン（γ－ＢＬ）、テトラヒドロフラン（ＴＨＦ）などの非水溶媒中に$LiClO_4$、$LiBF_4$、$LiAsF_6$、$LiPF_6$等のリチウム塩を溶解した非水電解液を用い、正極活物質としては主にTiS_2、MoS_2、V_2O_5、V_6O_{13}等の遷移金属の硫化物または酸化物を用いている。一方、非水電解液一次電池に用いられているMnO_2は、低コストであるという利点から、これを二次電池の正極活物質として用いることが考えられ、中でもスピネル構造の$LiMn_2O_4$は充放電の可逆性を有することが報告されている。
【０００３】
【発明が解決しようとする課題】しかしながら上述した$LiMn_2O_4$を正極活物質として用いた二次電池では、充放電でのサイクル寿命特性が劣るという問題があった。これを解決するために、例えば特開平２－１３９８６１号に
$(Li_{1-y}A_y)_x(Mn_{1-z}B_z)_2O_4$
A＝Na，K，Cu，Ag，Znから選ばれる元素
B＝V，Cr，Fe，Co，Niから選ばれる元素
$0.9 \leqq x \leqq 1.1$、$0.0 \leqq y \leqq 0.2$、$0.0 \leqq z \leqq 0.2$
で表される正極活物質、特開平３－１０８２６１号に$LiMn_2O_4$に２価金属イオン（例えばMg，Ca，Zn，Cd）を添加した正極活物質、
【０００４】特開平４－１６０７６９号に$LiMn_2O_4$結晶中のＭｎの一部をＣｏで置換し、
$Li_xMn_{2-y}M_yO_4$
M＝Co，Ni，Fe，Crから 選ばれる少なくとも１種の元素
$0.85 \leqq x \leqq 1.15$、$0.3 < y \leqq 0.5$で表される正極活物質が提案されており、いずれもその充放電でのサイクル寿命特性は改良されているが尚、十分ではなかった。本発明の課題は充放電でのサイクル寿命特性の優れた正極活物質及びこれを用いた非水電解液二次電池を提供することにある。

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【０００５】
【課題を解決するための手段】本発明は下記式で表される正極活物質及びこれを用いた非水電解液二次電池に係る。
$Li_{1+x}Mn_{2-x-y-z}AyBzO_4$
A＝Co，Ni，Fe，Crから選ばれる少なくとも１つの元素
B＝Mg，Zn，Caから選ばれる少なくとも１つの元素
$0 \leqq x \leqq 0.09$、$0.01 \leqq y \leqq 0.3$、$0.01 \leqq z \leqq 0.3$
【０００６】
【発明の実施の形態】本発明の上記式で表される正極活物質の製法の１例を以下に示す。例えば、$Li_{1+x}Mn_{2-x-y-z}Co_yMg_zO_4$で表される化合物は、Ｌｉ化合物、Ｍｎ化合物、Ｃｏ化合物、Ｍｇ化合物を所定の組成になるよう混合し、この混合物を加熱処理することにより得られる。ここでＬｉ化合物としては、例えばLi_2CO_3、$LiOH \cdot H_2O$、$LiNO_3$等を、Ｍｎ化合物としては、例えばMnO_2、Mn_3O_4、$MnCO_3$等を、Ｃｏ化合物としては、例えばCo_3O_4、$CoCO_3$、$Co(OH)_2$等を、Ｍｇ化合物としては、例えばMgO、$Mg(OH)_2$等を挙げることができる。加熱温度は通常約６５０～１０００℃の範囲であるが、７５０～９００℃の場合、さらに良好なサイクル寿命が得られるので好ましい。
【０００７】ここでＡ＝Co，Ni，Fe，Crから選ばれる少なくとも１つの元素、Ｂ＝Mg，Zn，Caから選ばれる少なくとも１つの元素であるが、これらのうち特にＡ＝Co，Ｂ＝Mgが好ましい。また$0 \leqq x \leqq 0.09$、$0.01 \leqq y \leqq 0.3$、$0.01 \leqq z \leqq 0.3$の範囲から選ばれるが、このうち$0 \leqq x \leqq 0.06$、$0.05 \leqq y \leqq 0.3$、$0.05 \leqq z \leqq 0.3$の範囲が好ましく、特に$0 \leqq x \leqq 0.03$、$0.1 \leqq y \leqq 0.2$、$0.1 \leqq z \leqq 0.2$の範囲が好ましい。
【０００８】本発明においては、上記正極活物質を用いて非水電解液二次電池を作成することができる。この非水電解液二次電池において、負極、電解液としては通常従来使用されているものを用いることができる。例えば負極としてはリチウム、リチウム化合物、リチウム合金、カーボン等を、電解液としてエチレンカーボネート（ＥＣ）、ジエチレンカーボネート（ＤＥＣ）、炭酸プロピレン（ＰＣ）、１，２－ジメトキシエタン（ＤＭＥ）、γ－ブチロラクトン（γ－ＢＬ）、テトラヒドロフラン（ＴＨＦ）などの非水溶媒中に$LiClO_4$、$LiBF_4$、$LiAsF_6$、$LiPF_6$等のリチウム塩を溶解した非水電解液を用いることができる。
【０００９】非水電解液二次電池の作成方法も通常従来使用されている方法をそのまま採用することができる。

本発明の上記正極活物質を用いて得られた非水電解液二次電池は優れた充放電でのサイクル寿命特性を有するもので、そのサイクル寿命は以下の実施例及び比較例より明らかなように、$LiMn_2O_4$の約６倍、$LiMn_{1.7}Co_{0.3}O_4$、$LiMn_{1.7}Mg_{0.3}O_4$の約１．５８～１．６４倍、更には２倍以上の顕著な効果を有する。

【００１０】

【実施例】以下に実施例および比較例を挙げて本発明を説明する。

実施例１～６および比較例１～７

Li_2CO_3，電解－MnO_2，Co_3O_4，MgOを所定の組成になるように秤量した後、乳鉢にて混合し、９００℃で１２時間焼成して表１に示される材料を合成した。得られた材料を粉末X線回折したところ図１，２に示されるように、$LiMn_2O_4$相が存在することが確認できた。さらに、材料 ０．８g、アセチレンブラック ０．１３g、ポリテトラフルオロエチレン ０．０７gを乳鉢にて混練し、厚さ ３０μmまで圧延した後、Niメッシュ（６０mesh）に圧着させ、１５０℃、１２時間の真空乾燥を行い、電池サイクル試験に用いた。電解液には１M $LiClO_4$＋５０%エチレンカーボネイト（ＥＣ）＋５０%ジ＊エチレンカーボネイト（ＤＥＣ）を、対極および参照極にはNiメッシュ（６０mesh）上にLi箔を圧着させたものを用いた。図３に電池試験に用いたセルを示す。電位範囲 ３．３～４．３Vvs.Li／Li^+，電流値は試料１g当たり４９．４mA、温度は２５℃とした。

【００１１】表１に充放電サイクル寿命を示す。$LiMn_2O_4$中のMnの一部をCoもしくはMgで置換しその置換量が増すごとにサイクル寿命が大きくなることが分かる。しかしCoとMgの２元素を同時に置換することにより、CoもしくはMgの１元素のみ置換した材料に比べさらにサイクル寿命が大きくなることが分かる。さらに、CoとMgの２元素を同時に置換した材料に、Li置換することにより、さらにサイクル寿命が大きくなることが分かる。このように、$LiMn_2O_4$中のMnの一部を１元素単独で置換を行うよりも、CoとMgの２元素、もしくはLi，Co、Mgの３元素で同時に置換することによりさらにサイクル寿命が向上することが分かる。尚、サイクル寿命は１サイクル目の放電容量の８０%に減少したときの寿命とし、そのサイクル数をいう。

【００１２】

【表１】

		組　成	サイクル寿命（サイクル数）
比較例	1	$LiMn_2O_4$	９２
	2	$LiMn_{1.9}Co_{0.1}O_4$	５８
	3	$LiMn_{1.8}Co_{0.2}O_4$	２５０
	4	$LiMn_{1.7}Co_{0.3}O_4$	３２０
	5	$LiMn_{1.9}Mg_{0.1}O_4$	７５
	6	$LiMn_{1.8}Mg_{0.2}O_4$	２６５
	7	$LiMn_{1.7}Mg_{0.3}O_4$	３３２
実施例	1	$LiMn_{1.9}Co_{0.05}Mg_{0.05}O_4$	５２５
	2	$LiMn_{1.8}Co_{0.1}Mg_{0.1}O_4$	６００以上
	3	$LiMn_{1.7}Co_{0.15}Mg_{0.15}O_4$	６００以上
	4	$Li_{1.02}Mn_{1.88}Co_{0.05}Mg_{0.05}O_4$	６００以上
	5	$Li_{1.08}Mn_{1.74}Co_{0.1}Mg_{0.1}O_4$	６００以上
	6	$Li_{1.00}Mn_{1.71}Co_{0.1}Mg_{0.1}O_4$	６００以上

【００１３】

【発明の効果】本発明では充放電でのサイクル寿命特性の優れた正極活物質及びこれを用いた非水電解液二次電池を提供することができる。

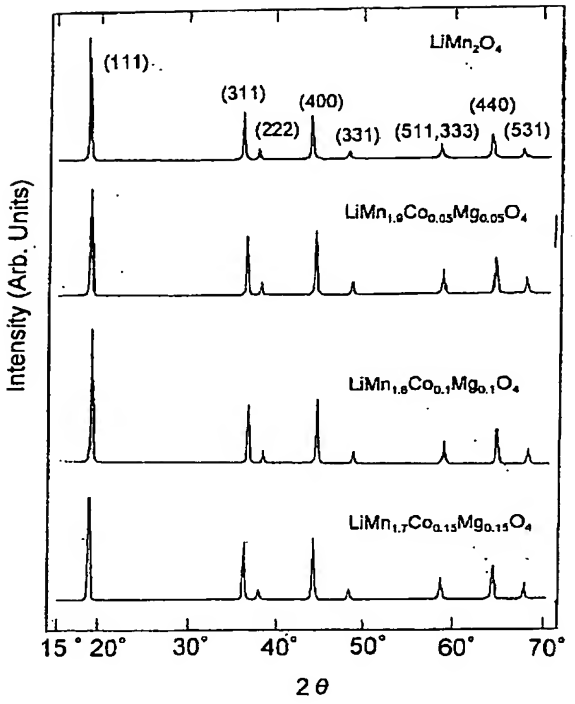
【図面の簡単な説明】

【図１】　$LiMn_2O_4$および実施例１～３で得られた正極活物質のX線回折図である。

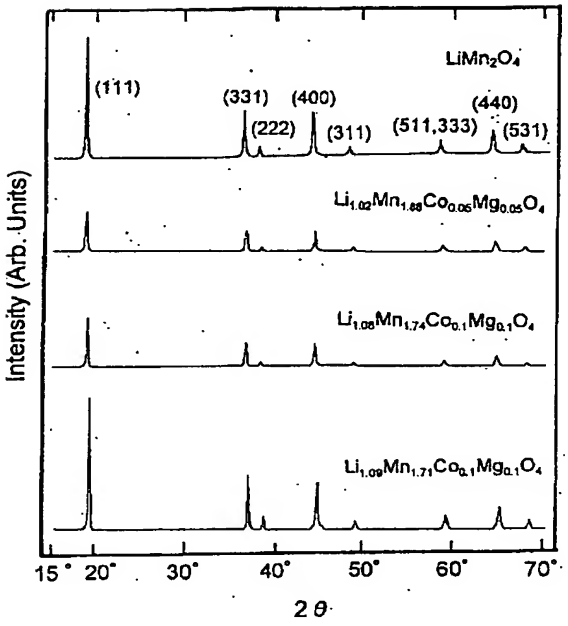
【図２】　$LiMn_2O_4$および実施例４～６で得られた正極活物質のX線回折図である。

【図３】　充放電サイクル試験に用いたセルを示す。

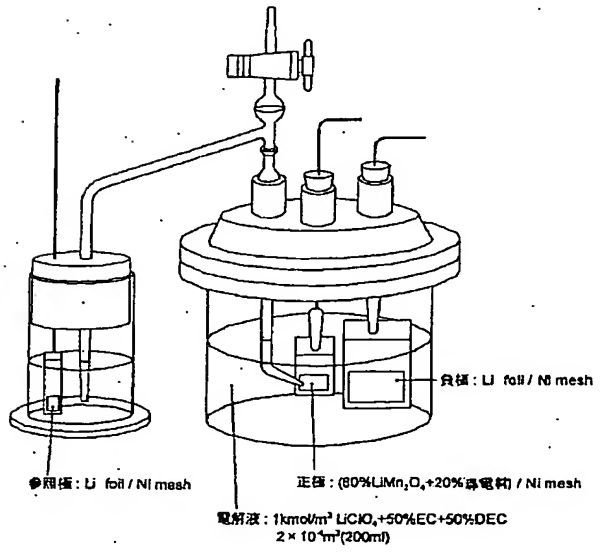
【図１】


LiMn2O4
(111)
(311)
(222)
(400)
(331)
(511,333)
(440)
(531)
LiMn1.9Co0.05Mg0.05O4
LiMn1.8Co0.1Mg0.1O4
LiMn1.7Co0.15Mg0.15O4
Intensity (Arb. Units)
15° 20° 30° 40° 50° 60° 70°
2θ

【図２】


LiMn2O4
(111)
(331)
(222)
(400)
(311)
(511,333)
(440)
(531)
Li1.02Mn1.88Co0.05Mg0.05O4
Li1.08Mn1.74Co0.1Mg0.1O4
Li1.09Mn1.71Co0.1Mg0.1O4
Intensity (Arb. Units)
15° 20° 30° 40° 50° 60° 70°
2θ

【図３】


負極：Li foil / Ni mesh
参照極：Li foil / Ni mesh
正極：(80%LiMn2O4+20%導電材) / Ni mesh
電解液：1kmol/m³ LiClO4+50%EC+50%DEC
2×10⁻⁴m³(200ml)

【手続補正書】
【提出日】平成１１年６月７日（１９９９．６．７）
【手続補正１】
【補正対象書類名】明細書
【補正対象項目名】請求項１
【補正方法】変更
【補正内容】
【請求項１】　下記式で表される正極活物質。
$Li_{1+x}Mn_{2-x-y-z}A_yB_zO_4$
A＝Co，Ni，Fe，Crから選ばれる少なくとも１つの元素
B＝Mg，　Caから選ばれる少なくとも１つの元素
０≦ｘ≦０．０９、０．０１≦ｙ≦０．３、０．０１≦ｚ≦０．３
【手続補正２】
【補正対象書類名】明細書
【補正対象項目名】０００５
【補正方法】変更
【補正内容】
【０００５】
【課題を解決するための手段】本発明は下記式で表される正極活物質及びこれを用いた非水電解液二次電池に係＊る。
$Li_{1+x}Mn_{2-x-y-z}A_yB_zO_4$
A＝Co，Ni，Fe，Crから選ばれる少なくとも１つの元素
B＝Mg，　Caから選ばれる少なくとも１つの元素
０≦ｘ≦０．０９、０．０１≦ｙ≦０．３、０．０１≦ｚ≦０．３
【手続補正３】
【補正対象書類名】明細書
【補正対象項目名】０００７
【補正方法】変更
【補正内容】
【０００７】ここでA＝Co，Ni，Fe，Crから選ばれる少なくとも１つの元素、B＝Mg，　Caから選ばれる少なくとも１つの元素であるが、これらのうち特にA＝Co，B＝Mgが好ましい。また０≦ｘ≦０．０９、０．０１≦ｙ≦０．３、０．０１≦ｚ≦０．３の範囲から選ばれるが、このうち０≦ｘ≦０．０６、０．０５≦ｙ≦０．３、０．０５≦ｚ≦０．３の範囲が好ましく、特に０≦ｘ≦０．０３、０．１≦ｙ≦０．２、０．１≦ｚ≦０．２の範囲が好ましい。

フロントページの続き

(72)発明者　真▲はな▼　愛子
兵庫県赤穂市中広1576　正同化学工業株式会社内

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5H014 AA02 HH00
5H029 AJ05 AK03 AL12 AM05 AM07 BJ01 HJ02

JAPANESE [JP,2000-048818,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

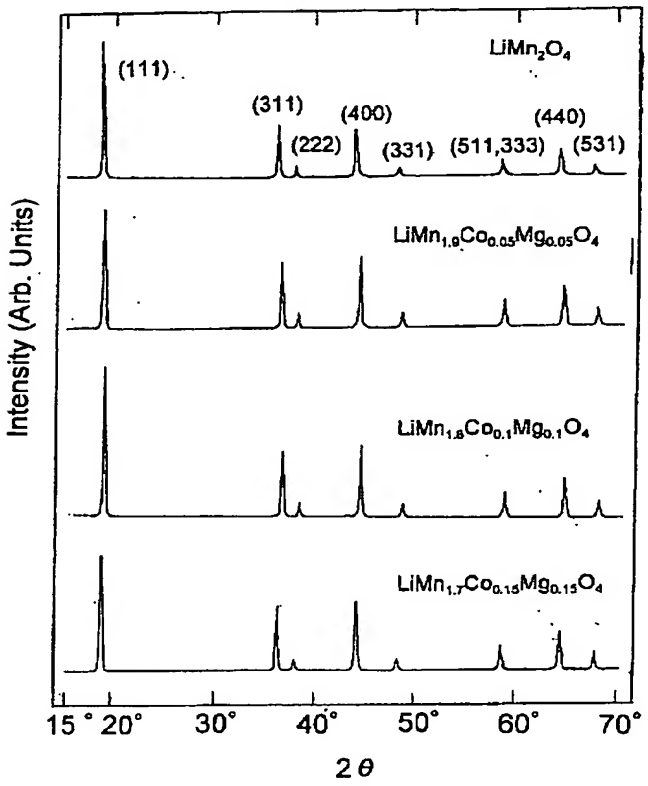
1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The positive active material expressed with the following formula.
Li1+xMn2-x-y-zAyBzO4 A=Co, at least one element B=Mg chosen from nickel, Fe, and Cr, at least one element $0<=x<=0.09$ chosen from Zn and calcium, $0.01<=y<=0.3$, $0.01<=z<=0.3$. [Claim 2] The nonaqueous electrolyte rechargeable battery using the positive active material of a claim 1.

[Translation done.]

Drawing selection drawing 1



[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte rechargeable battery using the positive active material and this which were improved.
[0002]
[Description of the Prior Art] A nonaqueous electrolyte rechargeable battery uses a lithium, a lithium compound, a lithium alloy, etc. for a negative electrode. As the electrolytic solution, a propylene carbonate (PC), 1, 2-dimethoxyethane (DME), The nonaqueous electrolyte which dissolved the lithium salt of LiClO4, LiBF4, LiAsF6, and LiPF6 grade is used into non-aqueous solvents, such as gamma-butyrolactone (gamma-BL) and a tetrahydrofuran (THF). As a positive active material, the sulfide or oxide of transition metals of TiS2, MoS2, V2O5, and V6O13 grade is mainly used. On the other hand, from the advantage that MnO2 used for the nonaqueous electrolyte primary cell is a low cost, it is possible to use this as a positive active material of a rechargeable battery, and it is reported especially that LiMn 2O4 of Spinel structure has the reversibility of charge and discharge.
[0003]
[Problem(s) to be Solved by the Invention] However, in the rechargeable battery using LiMn 2O4 mentioned above as a positive active material, there was a problem that the cycle-life property in charge and discharge was inferior. In order to solve this To for example, JP,2-139861,A The positive active material expressed with x(Mn1-zBz)2O4 A=Na, element B=V chosen from K, Cu, Ag, and Zn, the element 0.9<=x<=1.1 chosen from Cr, Fe, Co, and nickel, 0.0<=y<=0.2, and 0.0<=z<=0.2, (Li1-yAy) The positive active material, [0004] which added the divalent metallic ion (for example, Mg, calcium, Zn, Cd) to JP,3-108261,A at LiMn 2O4 A part of Mn under LiMn2O4 crystal is replaced by JP,4-160769,A by Co, and it is from LixMn2-yMyO4 M=Co, and nickel, Fe and Cr. At least one sort of elements 0.85<=x<=1.15 chosen and the positive active material expressed with 0.3< y<=0.5 were proposed, and although all were improved, they were not in addition enough. [of the cycle-life property in the charge and discharge] The technical problem of this invention is to offer the nonaqueous electrolyte rechargeable battery using the positive active material and this which were excellent in the cycle-life property in charge and discharge.
[0005]
[Means for Solving the Problem] this invention relates to the nonaqueous electrolyte rechargeable battery using the positive active material and this which are expressed with the following formula.
Li1+xMn2-x-y-zAyBzO4 A=Co, at least one element B=Mg chosen from nickel, Fe, and Cr, at least one element 0<=x<=0.09 chosen from Zn and calcium, 0.01<=y<=0.3, 0.01<=z<=0.3 [0006]
[Embodiments of the Invention] One example of the process of a positive active material expressed with the above-mentioned formula of this invention is shown below. For example, the compound expressed with Li1+xMn2-x-y-zCoyMgzO4 mixes Li compound, Mn compound, Co compound, and Mg compound so that it may become predetermined composition, and it is obtained by heat-treating this mixture. here -- as Li compound -- Li2CO3, LiOH-H2O, and LiNO3 grade -- as Mn compound -- MnO2, Mn 3O4, and MnCO3 grade -- as Co compound -- Co3 -- as a Mg compound, MgO and Mg(OH)2 grade can be mentioned for O4, CoCO3, and Co(OH)2 grade, for example Although it is usually the range of about 650-1000 degrees C, since a still better cycle life is acquired, in the case of 750-900 degrees C, heating temperature is desirable.
[0007] A=Co and B=Mg are [especially among these] desirable although it is at least one element chosen from A=Co, at least one element chosen from nickel, Fe, and Cr, B=Mg, and Zn and calcium here. Moreover, although chosen out of the range of 0<=x<=0.09, 0.01<=y<=0.3, and 0.01<=z<=0.3, the range of 0<=x<=0.06, 0.05<=y<=0.3, and 0.05<=z<=0.3 is desirable, and the range of 0<=x<=0.03, 0.1<=y<=0.2, and 0.1<=z<=0.2 is especially desirable.
[0008] In this invention, a nonaqueous electrolyte rechargeable battery can be created using the above-mentioned positive active material. In this nonaqueous electrolyte rechargeable battery, a negative electrode and the thing usually conventionally used as the electrolytic solution can be used. For example, the nonaqueous electrolyte which

dissolved a lithium, a lithium compound, a lithium alloy, carbon, etc. as a negative electrode, and dissolved the lithium salt of LiClO4, LiBF4, LiAsF6, and LiPF6 grade as the electrolytic solution into non-aqueous solvents, such as ethylene carbonate (EC), diethylene carbonate (DEC), a propylene carbonate (PC), 1, 2-dimethoxyethane (DME), gamma-butyrolactone (gamma-BL), and a tetrahydrofuran (THF), can be used.

[0009] The method by which the creation method of a nonaqueous electrolyte rechargeable battery is also usually used conventionally is employable as it is. The nonaqueous electrolyte rechargeable battery obtained using the above-mentioned positive active material of this invention has a cycle-life property in outstanding charge and discharge, and as for the cycle life, it has about 1.58 to 1.64 times of about 6 times of LiMn 2O4, LiMn1.7Co 0.3O4, and LiMn1.7Mg 0.3O4, and a remarkable effect more than double precision further so that more clearly than the following examples and examples of comparison.

[0010]

[Example] An example and the example of comparison are given to below, and this invention is explained to it. Examples 1-6 and the example 1 of comparison - 7Li2CO3, electrolysis - After carrying out weighing capacity of MnO2, Co3O4, and the MgO so that it may become predetermined composition, it mixed with the mortar and the material which calcinates at 900 degrees C for 12 hours, and is shown in Table 1 was compounded. When the powder X diffraction of the obtained material was carried out, as shown in drawing 1 and 2, it has checked that 2OLiMn4 phase existed. Furthermore, material 0.8g, acetylene black 0.13g, polytetrafluoroethylene 0.07g is kneaded with a mortar and it is thickness. After rolling out to 30 micrometers, you made it stuck to nickel mesh (60mesh) by pressure, 150 degrees C and the vacuum drying of 12 hours were performed, and it used for the cell cycle examination. The thing which stuck diethylene carbonate (DEC) to the electrolytic solution by pressure (ethylene carbonate EC) +50% 1M LiClO4+50%, and made Li foil stick to a counter electrode and a reference pole by pressure on nickel mesh (60mesh) was used. The cell used for the cell examination at drawing 3 is shown. Potential range 3.3-4.3Vvs.Li/Li+ and current value were made it to 49.4mA per 1g of samples, and temperature was made into 25 degrees C.

[0011] A charge-and-discharge cycle life is shown in Table 1. Whenever Co or Mg replaces a part of Mn in LiMn 2O4 and the amount of substitution increases, a cycle life is large and a bird clapper is known. However, compared with the material which replaced only one element of Co or Mg, a cycle life is still larger and by replacing two elements of Co and Mg simultaneously shows a bird clapper. Furthermore, by carrying out Li substitution, a cycle life is still larger and the material which replaced two elements of Co and Mg simultaneously understands a bird clapper. Thus, by replacing simultaneously a part of Mn in LiMn 2O4 by two elements of Co and Mg or three elements of Li, Co, and Mg rather than it replaces by 1 element independent shows that a cycle life improves further. In addition, a cycle life is made into the life when decreasing to 80% of the service capacity of 1 cycle eye, and says the number of cycles.

[0012]

[Table 1]

		組　成	サイクル寿命（サイクル数）
比較例	1	$LiMn_2O_4$	92
	2	$LiMn_{1.9}Co_{0.1}O_4$	58
	3	$LiMn_{1.8}Co_{0.2}O_4$	250
	4	$LiMn_{1.7}Co_{0.3}O_4$	320
	5	$LiMn_{1.9}Mg_{0.1}O_4$	75
	6	$LiMn_{1.8}Mg_{0.2}O_4$	265
	7	$LiMn_{1.7}Mg_{0.3}O_4$	332
実施例	1	$LiMn_{1.9}Co_{0.05}Mg_{0.05}O_4$	525
	2	$LiMn_{1.8}Co_{0.1}Mg_{0.1}O_4$	600以上
	3	$LiMn_{1.7}Co_{0.15}Mg_{0.15}O_4$	600以上
	4	$Li_{1.02}Mn_{1.88}Co_{0.05}Mg_{0.05}O_4$	600以上
	5	$Li_{1.06}Mn_{1.74}Co_{0.1}Mg_{0.1}O_4$	600以上
	6	$Li_{1.09}Mn_{1.71}Co_{0.1}Mg_{0.1}O_4$	600以上

[0013]

[Effect of the Invention] The nonaqueous electrolyte rechargeable battery using the positive active material and this which excelled [this invention] in the cycle-life property in charge and discharge can be offered.

[Translation done.]

* NOTICES *

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte rechargeable battery using the positive active material and this which were improved.

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PRIOR ART

[Description of the Prior Art] A nonaqueous electrolyte rechargeable battery uses a lithium, a lithium compound, a lithium alloy, etc. for a negative electrode, and is a propylene carbonate (PC) as the electrolytic solution. As a positive active material, the sulfide or oxide of transition metals of TiS2, MoS2, V2O5, and V6O13 grade is mainly used using the nonaqueous electrolyte which dissolved the lithium salt of LiClO4, LiBF4, LiAsF6, and LiPF6 grade into non-aqueous solvents, such as 1, 2-dimethoxyethane (DME), gamma-butyrolactone (gamma-BL), and a tetrahydrofuran (THF). On the other hand, from the advantage that MnO2 used for the nonaqueous electrolyte primary cell is a low cost, it is possible to use this as a positive active material of a rechargeable battery, and it is reported especially that LiMn 2O4 of Spinel structure has the reversibility of charge and discharge.

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EFFECT OF THE INVENTION

[Effect of the Invention] The nonaqueous electrolyte rechargeable battery using the positive active material and this which excelled [this invention] in the cycle-life property in charge and discharge can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in the rechargeable battery using LiMn 2O4 mentioned above as a positive active material, there was a problem that the cycle-life property in charge and discharge was inferior. In order to solve this To for example, JP,2-139861,A The positive active material expressed with x(Mn1-zBz)2O4 A=Na, element B=V chosen from K, Cu, Ag, and Zn, the element 0.9<=x<=1.1 chosen from Cr, Fe, Co, and nickel, 0.0<=y<=0.2, and 0.0<=z<=0.2, (Li1-yAy) The positive active material which added the divalent metallic ion (for example, Mg, calcium, Zn, Cd) to JP,3-108261,A at LiMn 2O4, [0004] A part of Mn under LiMn2O4 crystal is replaced by JP,4-160769,A by Co, and it is from LixMn2-yMyO4 M=Co, and nickel, Fe and Cr. At least one sort of elements 0.85<=x<=1.15 chosen and the positive active material expressed with 0.3< y<=0.5 were proposed, and although all were improved, they were not in addition enough. [of the cycle-life property in the charge and discharge] The technical problem of this invention is to offer the nonaqueous electrolyte rechargeable battery using the positive active material and this which were excellent in the cycle-life property in charge and discharge.

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MEANS

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EXAMPLE

[Example] An example and the example of comparison are given to below, and this invention is explained to it. Examples 1-6 and the example 1 of comparison - 7Li2CO3, electrolysis - After carrying out weighing capacity of MnO2, Co3O4, and the MgO so that it may become predetermined composition, it mixed with the mortar and the material which calcinates at 900 degrees C for 12 hours, and is shown in Table 1 was compounded. When the powder X diffraction of the obtained material was carried out, as shown in drawing 1 and 2, it has checked that 2OLiMn4 phase existed. Furthermore, material 0.8g, acetylene black 0.13g, polytetrafluoroethylene 0.07g is kneaded with a mortar and it is thickness. After rolling out to 30 micrometers, you made it stuck to nickel mesh (60mesh) by pressure, 150 degrees C and the vacuum drying of 12 hours were performed, and it used for the cell cycle examination. The thing which stuck diethylene carbonate (DEC) to the electrolytic solution by pressure (ethylene carbonate EC) +50% 1M LiClO4+50%, and made Li foil stick to a counter electrode and a reference pole by pressure on nickel mesh (60mesh) was used. The cell used for the cell examination at drawing 3 is shown. Potential range 3.3-4.3Vvs.Li/Li+ and current value were made it to 49.4mA per 1g of samples, and temperature was made into 25 degrees C.

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[0012]

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	7	$LiMn_{1.7}Mg_{0.3}O_4$	332
実施例	1	$LiMn_{1.9}Co_{0.05}Mg_{0.05}O_4$	525
	2	$LiMn_{1.8}Co_{0.1}Mg_{0.1}O_4$	600以上
	3	$LiMn_{1.7}Co_{0.15}Mg_{0.15}O_4$	600以上
	4	$Li_{1.02}Mn_{1.88}Co_{0.05}Mg_{0.05}O_4$	600以上
	5	$Li_{1.05}Mn_{1.74}Co_{0.1}Mg_{0.1}O_4$	600以上
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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the X diffraction view of the positive active material obtained in LiMn 2O4 and the examples 1-3.
[Drawing 2] It is the X diffraction view of the positive active material obtained in LiMn 2O4 and the examples 4-6.
[Drawing 3] The cell used for the charge-and-discharge cycle examination is shown.

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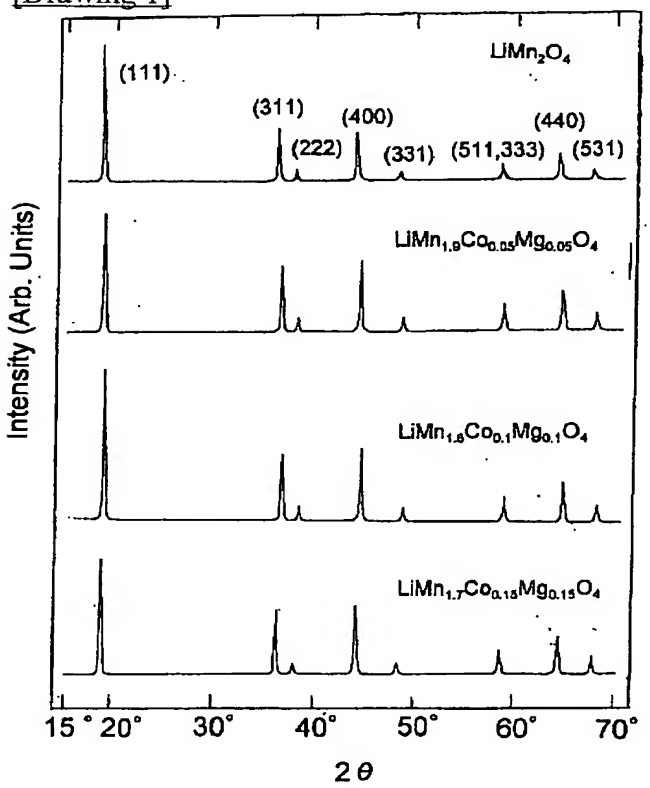
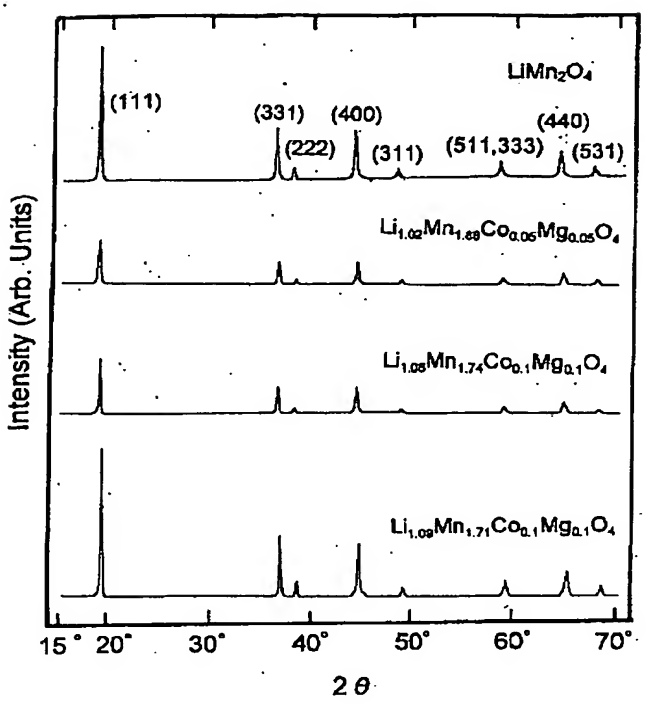
DRAWINGS

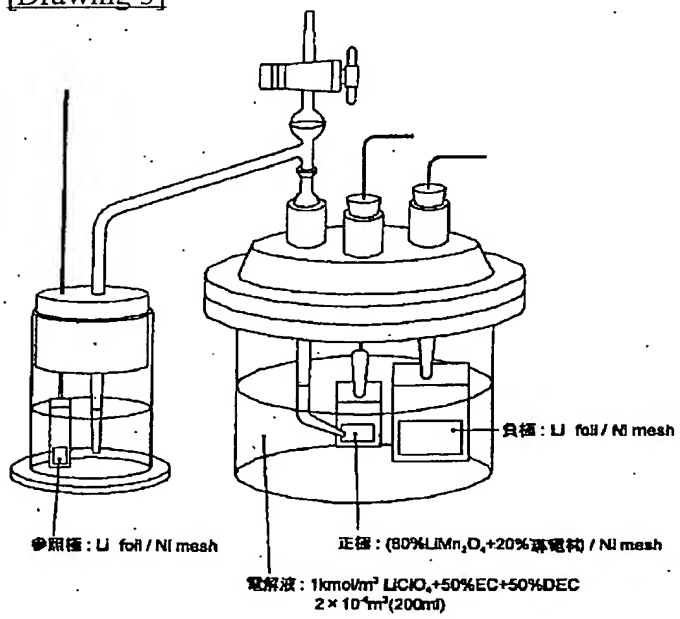
[Drawing 1]



[Drawing 2]



[Drawing 3]



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